Development of conductive supramolecular anion radical salts containing halogen-based supramolecular interactions

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Novel conductive supramolecular anion radical salts containing halogen-based supramolecular interactions have been obtained from galvanostatic oxidation of acceptor molecules with dihalo-pyridinium cations. The dihalo-pyridinium cations were prepared by reactions of dihalo-pyridines with the Meerwein reagent or alkyl halide. For obtained single crystals, (Me-3,5-DIP *N*-methyl-3,5-diiodopyridinium; (Me-3,5-DIP)(TCNQ)<sub>2</sub> 1 = **TCNO** = 7,7,8,8-tetracyanoquinodimethane) and (Me-3,5-DBP)[Ni(dmit)<sub>2</sub>]<sub>2</sub> 2 (Me-3,5-DBP = N-methyl-3,5-dibromopyridinium; dmit = 1,3-dithiol-2-thione-4,5-dithiolate), were performed X-ray crystal structure analyses and measurements of electrical resistivity. In 1, TCNQ anions form one-dimensional column structure. I...N interactions between the cation and the TCNQ anion are observed. The distances are 5 % shorter than the sum of the van der Waals radii. The electrical resistivity shows semiconductive behavior due to the charge separation of the TCNQ anions. The  $Ni(dmit)_2$  anions in 2 form one-dimensional column structure. Short contacts between the cation and Ni(dmit)<sub>2</sub> anions are also observed. The Br…S distances are more than 10 % shorter than the sum of the van der Waals radii. This is the first conducting Ni(dmit)<sub>2</sub> salt containing the supramolecular Br...S interaction. The electrical resistivity behaves semiconductive, which is consistent with the result of the tight-binding band calculation.

